anywhere from within the lower sub-band to the lower edge of the upper sub-band.

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NMR study of 2, 4—dihydroxy benzoic acid

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Nuclear Magnetic Resonance studies of 2,4-dihydroxy benzoic acid popularly known as β-resorcylic acid have been made in the temperature range 77°K to 383°K. An agreement has been observed between the experimental values of proton second moment obtained from the derivative curves of the PMR absorption line for the compound and the calculated value of the proton second moment for rigid lattice, indicating that the lattice is rigid up to the transition temperature. A reduction in the value of proton second moment has been explained as due to the random motion of the hydroxy groups.

The measurement of the variation of NMR absorption lines with temperature in a solid can give valuable information regarding various molecular motions and diffusion process which may be occurring in the compound (Gutowsky & Pake 1950).

The crystal structure of 2,4-dihydroxy benzoic acid was determined by Giacomello *et al* (1956) by a molecular Fourier transform method. The four molecules in a unit cell are arranged in two centrosymmetric dimers related by the center of symmetry of the P_1^- space group. The crystal data : $a = 7{\cdot}05$Å, $b = 9{\cdot}67$Å, $c = 11{\cdot}81$Å, $\alpha = 98°50'$, $\beta = 109°28'$, $\gamma = 91°43'$ and $z = 4$.

The positional coordinates of the hydrogen atoms of 2,4-dihydroxy benzoic acid were not given and so they were calculated by authors.

The NMR experiment was performed using a Varian Associates variable frequency spectrometer and a 12″ magnet system. The records were observed at 7·5 Mc/Sec. at Tata Institute of Fundamental Research, Bombay. The experiment was performed over temperature range from 77°K to 383°K.

Theoretical rigid lattice value of proton second moment was calculated from the expression based on Van Vleck's theory (Van Vleck 1948, Bearden & Watts 1951) for a polycrystalline sample.

The intra molecular contribution for protons is given as

$$S_1 = \frac{715{\cdot}9}{N} \sum_{j<k} r_{jk}^{-6} G^2$$

where N is the number of magnetic nuclei over which the sum is taken, and r is the internuclear distance between the nuclei j and k.

The intra molecular contribution to the proton second moment thus calculated for the compound and estimated to be about $6{\cdot}88G^2$.

The intermolecular contribution S_2 to the proton second moment was calculated following the method adopted by Andrew & Eades (1953) and estimated to be about $6{\cdot}10G^2$. The value seems to be reasonable as compared to $6{\cdot}8G^2$, the intermolecular contribution to the proton second moment for substituted benzoic acids calculated by Agarwal *et al* (1974).

At 77°K the mean value of experimental proton second moment is $12{\cdot}14 \pm 1G^2$ which is in good agreement with the theoretically evaluated value ($S_1 + S_2 = 12{\cdot}98$ G^2). This implies that the lattice is effectively rigid at lower temperature.

The variation of the proton second moment against temperature is shown in figure 1. The value of proton second moment at room temperature 294·5°K was reduced to $7{\cdot}10G^2$. Alpert (1947) and Gutowsky & Pake (1950) studied in detail the effect of motion in the lattice following the theory given by Bloembergen *et al* (1948). The re are three possibilities to account this reduction (1) the molecular reorientation, (2) the rotation of COOH group, (3) the rotation of hydroxy groups.

The possibility of molecular reorientation is completely ruled out due to fairly large size of the molecule and also disagreement with the theory given by Gutowsky & Pake (1950).

If the possibility of reorientation of COOH group is considered, only COOH contribution to the proton second moment will be affected, which can easily be estimated using the method of Moskalev (1962). It is found that for COOH group reorientation a reduction of only about $2{\cdot}4G^2$ will be observed. Whereas, in our observation, the proton second moment is found to be $7{\cdot}10G^2$ as against

its rigid lattice value $12{\cdot}15G^2$ i.e., a reduction of $5{\cdot}04G^2$. This indicates that the decrease in the proton second moment value is not due to reorientation of COOH group.

For the investigation of third possibility i.e., reorientation of hydroxy groups, it is noted that the OH group rotation would only affect the OH group contribution to the proton second moment (1974). OH group rotation should reduce the OH group contribution to S_1 by a factor of 0·87 (Smith 1969). OH–OH contribution was found to be $1{\cdot}79G^2$ and by OH group rotation, it will be reduced by $1{\cdot}55G^2$. The reduced S_1 would be $5{\cdot}33G^2$.

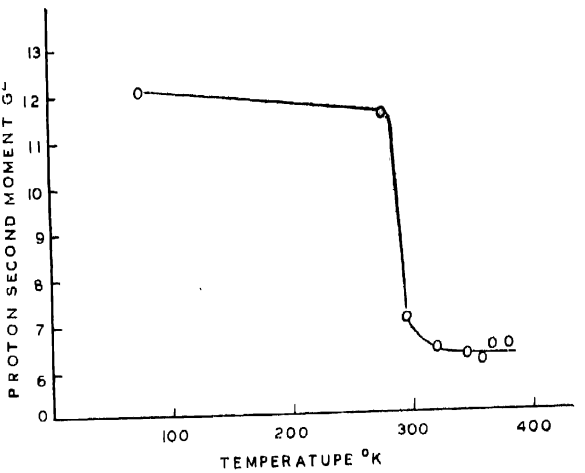

Fig. 1. Graph showing variation of proton second moment with temperature.

The estimation of the reduced intermolecular contributions can be made making use of reduction factors. Smith (1965) has given a range of reduction factors of 0·65–0·5 for stationary-rotating interation and 0·42–0·25 for rotating-rotating interaction. If we consider both the OH groups to be freely rotating then using the reduction factors we find that intermolecular contribution should lie in the range $2{\cdot}56G^2$–$1{\cdot}52G^2$. Thus the reduced value of proton second moment should lie in the range $7{\cdot}89$–$6{\cdot}85G^2$. The experimentally observed value $7{\cdot}10G^2$ actually lies in this range. This confirms that the reduction in proton second moment is due to reorientation of hydroxy groups.

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Study of island growth in vapour deposited lead sulphide films by optical diffraction from the electron micrograph.

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Study of the properties of vapour deposited lead sulphide films is of importance because of their applications in devices as infra-red detectors. Since most of the magnetic, electrical and optical properties of polycrystalline films depend critically on the thickness and microstructure, a study of the structural characteristics of the films would be highly useful. The use of small angle X-ray scattering and small angle electron diffraction for determining the particle sizes and size-distributions is well known (Guinier & Fournet 1955, Ferrier 1969). Beeston *et al* (1972) have reviewed the various studies on the optical diffraction from electron micrographs and have emphasised its uses in obtaining structural information. Hence in the present investigation, the island sizes have been determined by the optical diffraction from the electron micrographs and also by the conventional technique. Preferred orientation and the sizes of the coherently diffracting crystallites have been determined by X-ray line broadening method.

Thin films of different thickness were deposited on glass substrates kept at room temperature using an Edwards Vacuum coating unit under a vacuum of 10^{-5} torr. The thickness of the films was estimated by the loss of mass method. The surface structures of the PbS films used in the present investigation were studied by the carbon replica technique. For obtaining better contrast the